

Synthesis and characterization of silica–titania core–shell particles

SUCHITA KALELE¹, RAVI DEY¹, NEHA HEBALKAR¹, J URBAN²,
S W GOSAVI¹ and S K KULKARNI^{1,*}

¹Department of Physics, University of Pune, Pune 411 007, India

²Fritz-Haber Institute, Faradayweg 4-6, 14195 Berlin, Germany

*Corresponding author. E-mail: skk@physics.unipune.ernet.in

Abstract. Nearly monodispersed particles of silica were prepared and coated with uniform layers of titanium dioxide in anatase phase by hydrolysis and condensation of titanium butoxide. The coating thickness could be altered by adjusting the concentration of reactants (titanium butoxide and water) and the amount of added silica particles. Different coating thicknesses were deposited and studied using optical absorption spectroscopy, electron microscopy and Fourier transform infra-red spectroscopy. It was found that silica particles of size 170 ± 5 nm were coated with 23 ± 5 nm thick layer of titanium dioxide. Alternatively titania particles of size 340 ± 5 nm were synthesized by controlled hydrolysis of titanium ethoxide in the presence of sodium chloride. These particles were further coated with 135 ± 5 nm thick layer of silica to investigate changes in properties after changing the shell material.

Keywords. Core–shell particles; silica particles; titania particles; transmission electron microscopy.

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1. Introduction

Core–shell particles constitute a novel class of materials with potential applications in chemically stabilizing colloidal particles, catalysis, fluorescent diagnostics, photonic band-gap materials, preparation of bioconjugates etc [1]. These particles can be synthesized using metals, semiconductors, insulators, metal oxides, alloys, dyes and even biomolecules as core or shell.

Core–shell particles of silica–titania have many applications. Titania is one of the most important photocatalyst, but it is thermally unstable. Uniform coating of titania onto silica can enhance its stability and catalytic activity. It is also an interesting photonic band-gap material. Low refractive index of silica (1.48) and high refractive index of titania (2.5) produces substantial modulation of dielectric medium when organized as a two- or three-dimensional crystal.

There are several reports on coating of titania on silica [2] and vice versa [3] which showed that such coatings were possible. However, attempts were made only to

synthesize these particles but details of analysis were lacking. Silica-coated titania particles are not studied in detail except in ref. [3] which does not include the details of synthesis procedure. We have synthesized these core-shell particles using an approach described in ref. [2] but have carried out detailed investigations on the nature of coatings, their homogeneity and structure. The studies were also carried out by exchanging the core and shell materials to investigate change in the properties. The presence of shell is analysed by UV-Vis absorption spectroscopy, Fourier transform infra-red spectroscopy (FTIR) and transmission electron microscopy (TEM).

2. Experimental

Silica and titania particles were separately synthesized by sol-gel method and coated with respective shell materials in a multistep process. Details of synthesis and analysis techniques are given below.

2.1 Synthesis of titania-coated silica particles

Silica particles were synthesized using Stöber method by hydrolysis and condensation of TEOS (tetraethylorthosilicate) ($\text{Si}(\text{OC}_2\text{H}_5)_4$). Uniform layers of titania were deposited by controlled hydrolysis of titanium butoxide in the presence of silica particles. Titanium butoxide (0.2 ml), water (0.48 ml) and ethanol (50 ml) were mixed with weighted amount (0.1 g dispersed in 30 ml of ethanol) of silica particles. The mixture was refluxed at 80°C for 90 min to get white precipitate. The precipitate was washed with ethanol and dried.

2.2 Synthesis of silica-coated titania particles

Titania particles were synthesized by sol-gel method [4]. For coating titania particles with silica, hydrolysis of TEOS was carried out in the presence of titania particles. Silica shell grows on such titania nuclei. To a mixture of ethanol (15 ml), ammonium hydroxide (0.75 ml) and water (3 ml), dispersion of titania particles (0.05 g particles in 10 ml ethanol) was added and total mixture was stirred for 30 min. TEOS (1.2 ml) was added and the mixture was stirred for 180 min. The dispersion was centrifuged and washed with ethanol and dried.

3. Characterization

Optical absorption of the particles was studied using ocean optics (model DT 1000 CE 376) spectrophotometer in the range 200–800 nm. Fourier transform infra-red spectroscopy was performed with Shimadzu 8400 spectrophotometer. Particle morphology was studied using transmission electron microscopy (TEM) using Philips CM 200 FEG microscope.

4. Results and discussion

Silica is widely used as either core or shell material because of its easy formation. Titania coatings are exceptionally difficult to synthesize because titania precursors are highly reactive. They hydrolyse so fast that it is difficult to control their precipitation. Uniform coating of titania on silica particles is obtained under limited set of conditions. The ratio of titanium butoxide to water and dilution of reaction mixture in ethanol control the coating nature. If the butoxide concentration is too high, separate titania particles are formed. Higher water concentration leads to aggregated spheres connected with titania neck. If the ratio of silica particles in the reaction mixture is greater than titanium alkoxide concentration, then all the particles are not covered with titania properly. Therefore the ratio of silica particles and titania precursor was adjusted so that uniform coating can be obtained.

Optical absorption spectra of silica particles (curve A), titania-coated silica particles (curve B), titania particles (curve C) and silica-coated titania particles (curve D) are shown in figure 1. Silica particles do not show any optical absorption peak between 200 and 800 nm, while spherical titania particles of size 340 nm show an absorption peak at 328 nm. Titania-coated silica particles show a broad absorption peak at 320 nm. The peak indicates that silica particles are coated with titania. Interestingly, when titania particles were coated with silica, absorption peak broadens and shifts to longer wavelength (348 nm), indicating the increase in size of particles. Presence of silica coating is confirmed by increase in size of particles.

Figure 2 shows the FTIR spectra of silica particles (curve A), titania-coated silica particles (curve B), titania particles (curve C) and silica-coated titania particles (curve D). For silica particles (curve A), peaks at 1112 cm^{-1} and 801 cm^{-1} indicate the presence of Si–O–Si bond. The peak at 949 cm^{-1} indicates the presence of Si–OH bond. Intensity of these peaks has reduced significantly after coating with titania. Also titania-coated silica particles (shown in inset) show small peaks at

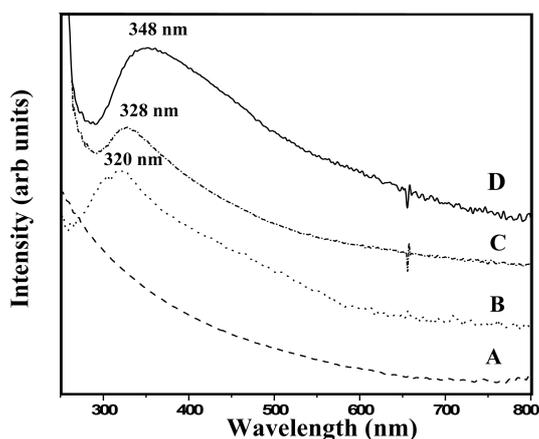


Figure 1. UV–Vis absorption spectra of silica particles (curve A), titania-coated silica particles (curve B), titania particles (curve C) and silica-coated titania particles (curve D).

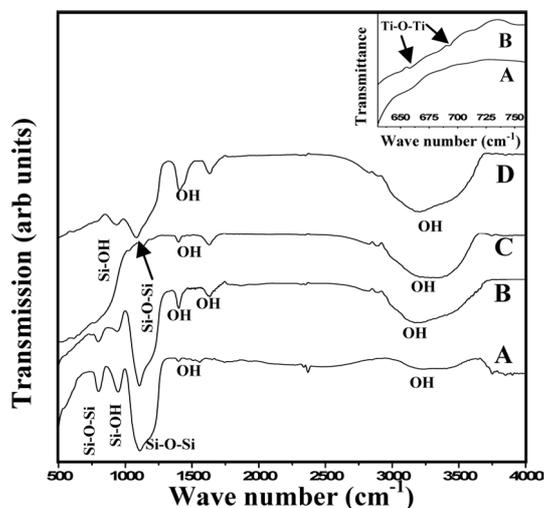


Figure 2. FTIR spectra of silica particles (curve A), titania-coated silica particles (curve B), titania particles (curve C), silica-coated titania particles (curve D). Inset shows FTIR spectra of silica particles (curve A) and titania-coated silica particles (curve B) in the range 625–750 cm^{-1} .

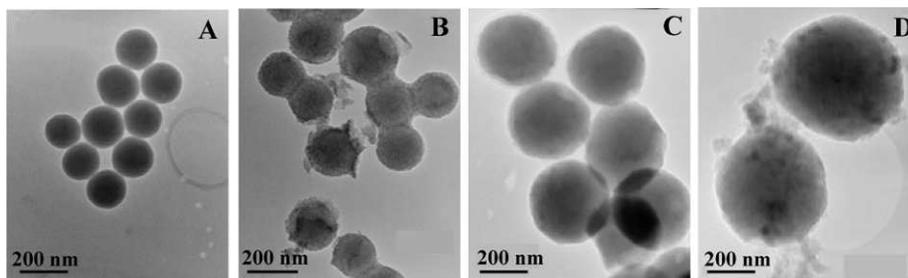


Figure 3. TEM images of overview of (A) silica particles, (B) titania-coated silica particles, (C) titania particles and (D) silica-coated titania particles.

685 cm^{-1} and 653 cm^{-1} which belong to Ti–O–Ti bonding. These peaks are absent in the case of uncoated silica particles. Comparison of FTIR spectra of titania particles (curve C) and silica-coated titania particles (curve D) reveals that coating is successfully done. Titania particles did not show any peaks at 1083 and 935 cm^{-1} while these peaks are seen in silica-coated titania particles. These peaks belong to Si–O–Si and Si–OH bond respectively indicating the presence of silica on titania particles.

The direct way of observing the coatings is by using transmission electron microscopy (TEM). Figure 3 shows TEM images of (A) silica particles, (B) titania-coated silica particles, (C) titania particles and (D) silica-coated titania particles. Image (A) shows silica particles of average size 170 ± 5 nm having very smooth and clean surfaces. After coating these particles with titania (image B) their surfaces appear rough and particles start agglomerating together. In this case, particles of

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size 201 ± 5 nm and coating thickness of 23 ± 5 nm were obtained. High resolution TEM image and electron diffraction image (not shown here) revealed that silica particles are amorphous in nature while titania coatings are crystalline in nature having anatase phase of titania. EDAX analysis revealed that silica particles were having Si (35%) and O (65%) atomic composition. For titania-coated silica particles the % atomic composition was found to be Si (31.5%), Ti (10.9%) and O (57.6%). Image (C) shows TiO_2 particles of size 340 nm. These particles were coated with silica (D) and after coating the particle size obtained was around 475 ± 5 nm having coating thickness around 135 ± 5 nm.

5. Conclusions

Silica particles of size around 170 ± 5 nm were prepared and coated with homogeneous layers of titania in anatase phase. The coating thickness was found to be around 23 ± 5 nm. Alternatively titania particles of size around 340 ± 5 nm were synthesized and coated with 135 ± 5 nm thick layer of silica. The presence of coating was detected using optical absorption spectroscopy, FTIR spectroscopy and electron microscopy.

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